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# **Functional nanomaterials to augment photosynthesis: evidence and considerations for their responsible use in agricultural applications**

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**At the current population growth rate, we will soon be unable to meet increasing food demands. As a consequence of this potential problem, considerable efforts have been made to enhance crop productivity by breeding, genetics and improving agricultural practices. Whilst these techniques have traditionally been successful, their efficacy since the “green revolution” have begun to significantly plateau. This stagnation of gains combined with the negative effects of climate change on crop yields has prompted researchers to develop novel and radical methods to increase crop productivity. Recent work has begun exploring the use of nanomaterials as synthetic probes to augment how plants utilise light. Photosynthesis in crops is often limited by their ability to absorb and exploit solar energy for photochemistry. The capacity to interact with and optimise how plants use light has the potential to increase the productivity of crops and enable the tailoring of crops for different environments and to compensate for predicted climate changes. Advances in the synthesis and surface modification of nanomaterials have overcome previous drawbacks and renewed their potential use as synthetic probes to enhance crop yields. Here, we review the current applications of functional nanomaterials in plants and will make an argument for the continued development of promising new nanomaterials and future applications in agriculture. This will highlight that functional nanomaterials have the clear potential to provide a much-needed route to enhanced future food security. In addition, we will discuss the often-ignored current evidence of nanoparticles present in the environment as well as inform and encourage caution on the regulation of the nanomaterials in agriculture.**

Continued population growth has dramatically increased our productivity demands on each hectare of farmland [1,2]. Simultaneously, this has been compounded by a background of losses of farmland due to urbanisation and soil degradation; the transition of land usage from grain to meat or biofuels due to changing global diets and energy demands; greater uncertainty on yields due to climate change; and numerous other factors [3–6]. This has resulted in scientists stating the startling and troubling statistics that we may be as close as one crop cycle away from food shortages and that we may need to double our

global crop yields by 2050 [1,7]. The world is currently dependent on four major crops: maize (*Zea mays*), rice (*Oryza sativa*), wheat (*Triticum aestivum* and *Triticum durum*) and soybean (*Glycine max*) [7]. All of these crops have seen a plateau in their yearly increase in productivity following the green revolution [1,3,7,8]. Combined, these factors have made enhancing the productivity per hectare of the four major crops the primary challenge facing agricultural science [1,7].

Previous increases in crop yield have primarily come from three major sources: Mendelian breeding, improving farming practices and targeted modification of genes [9]. One of the most obvious examples of these methods is the development of dwarfism in wheat during the “green revolution” for which Norman Borlaug was awarded the Nobel peace prize in 1970 [10]. Dwarfism has dramatically increased productivity for two reasons: reduced energy dedicated to non-yield biomass and decreased lodging [11–13]. Another important way in which key crop productivity has been enhanced is by extending the growing season of, most crops do not use the full potential of their growing season in their specific location and this has been notably exploited with maize [14–16]. Although these routes have historically been very successful, they are beginning to reach the limits of their efficacy as most of the potential gains by these techniques have already been realised [9].

Historically, researchers have avoided, or were hesitant of attempts to increase photosynthetic efficiency by modifying how plants utilise light based on the hypothesis that it could not enhance the biomass yield [2,9,17]. Over the last 15 years this has repeatedly been shown to be incorrect, as has been summarised in several reviews [7,9,17,18]. A key motivator for researchers to enhance photosynthetic efficiency is that plants greatly underperform compared to their theoretical potential [2]. This can be a consequence of recent climate change that crop has yet to adapt to; plant evolution not always being driven by maximal photosynthetic-efficiency; and other factors such as being grown in sub-optimal environments [19]. As a result of these inefficiencies, crop systems are not light-limited for the majority of the day and are instead limited by the rate of other downstream molecular and photochemical processes [9,20]. This is compounded by the fact that even though crop plants can absorb up to 90% of the wavelengths within visible spectrum that is incident on their leaves, they transmit the majority of the rest of the solar spectrum which accounts for over half of the energy incident on a leaf [21]. It is now well established that high light intensities pose a significant risk to plants, and generate reactive oxygen species, as the electron transport chain is unable to keep pace with light harvesting and charge-separation and prevent formation of reactive oxygen species (ROS) [20,22] and the resulting photo-damage and photo-inhibition. To counter these potentially deleterious photochemically induced reactions, plants have a rapidly reversible suite of photo-protection mechanisms, termed non-photochemical quenching (NPQ) that serve to dissipate excess energy harnessed from light harvesting and dissipate it harmlessly as heat [22]. Although it has been shown to be possible to augment photosynthesis and initiate enhanced yields

in field conditions, we note that the observed increase in productivity is often less than the boost in photosynthesis [9]. This is probably due to the inability of plants to utilise the enhanced photosynthate, suggesting there may also be advantages to modulating the efficacy of utilisation of photosynthate [7].

As the solar light absorption is often detuned from its maximal point due to harmful photochemistry, researchers have identified that increasing the electron transport out from the photosystems is beneficial via optimising ATP synthesis and the Calvin cycle to enhance photosynthesis [23,24]. Consequently, the over-expression of the Reiske protein, which stimulates cyclic electron transport driving the production of ATP but excluding PSII and thus limiting the risk of PSII dependent ROS production, has been shown to increase biomass and seed yields in *Arabidopsis thaliana* [25]. In many cases plants also have down-regulated levels of the photosynthetic enzymes, thus lowering the limit of their theoretical maximum efficiency [23]. Notably this has been modelled and exploited by the transgenic over-expression of the limiting Calvin cycle enzymes such as sedoheptulose-1,7-bisphosphatase (SBPase), fructose 1,6-bisphosphate aldolase (FBPA) and fructose 1,6-bisphosphate aldolase (GDC-H) in key plant species to give a significant increase in crop productivity and adapting them to deal with climate change [26–29]. This method of transgenic overexpression results in an additive effect, meaning that the triple-mutant overexpressing each of these enzymes can produce over-70% more biomass [29]. It is also possible to directly manipulate the initial reactions in photosynthesis: overexpression of the photosystem II subunit-S (PsbS), a component of the major light-harvesting complex that also performs the oxidation of water, may lead to an increase water use efficiency. This is a significant limiting component in many agricultural settings and drives greater yields in *N. tabacum* [30]. There are limitations in photo-protection, NPQ, that may also be exploited with recent work showing that that accelerating the kinetics of the xanthophyll cycle, a cycle that modulates a key radical scavenging carotenoid between active and inactive photo-protective forms in light harvesting antenna of PSII, can enhance the response of NPQ to variable light conditions. This was achieved by the transgenic overexpression of the enzymes violaxanthin de-epoxidase (VDE) and zeaxanthin epoxidase (ZE) which led to a dramatic 15% increase in productivity in field conditions in *Nicotiana tabacum* by reducing unnecessary NPQ immediately after high-intensity illumination [31]. While these changes lead to phenomenal increases in productivity, there are still issues associated with genetic modification, particularly of food crops.

A contrasting, yet often sensible approach is to take inspiration from natural systems in the form of bio-mimicry. There is a diverse range of natural examples of organisms and systems manipulating how they interact with light to enhance photosynthesis. One of the most elegant of these systems is a symbiotic relationship between zooxanthellae and coral. In this system, the non-photosynthetic symbiont (the coral) harvests light and modulates the temperature for the photosynthetic symbiont (zooxanthellae). These

organisms live at depths of up to 145 m where there is traditionally too low light intensities for photosynthesis [32]. To overcome this the coral having evolved fluorescent light-harvesting mechanisms to provide additional light for their symbiont algae [33–38]. A similar system is present in the giant clams, *Tridacna crocea*, which have developed highly-reflective cells named iridocytes which do not produce colour using chemical pigments but instead use structural colour caused by physical photonic structures at the nanoscale that act as Bragg reflectors and illuminate the symbiotic algae present in the clam [39–41]. These observations suggest that it is possible that other forms of structural colour produced *in planta* have evolved to enhance photosynthesis or photo-protection in specific lighting environments. These photonic structures are often highly reflective and their colour can be angularly dependent, which is known as iridescence. There are an extraordinary phylogenetically diverse range of photosynthetic organisms that exhibit structural colour within their photosynthetic tissue including: the spikemoss *Selaginella willdenowii*; tropical ferns *Danaea nodosa*, *Trichomeanes elegans* and *Diplazium tomentosum*; the red algae *Chondrus crispus*; the diatom *Coscinodiscus granii* and the angiosperm *Begonia pavonina* [42–49]. Currently researchers are beginning to establish the links between these various photonic structures and photosynthesis. Notably, recently Jacobs *et al.* demonstrated that the iridescent modified chloroplasts (iridoplasts) present in the epidermis of *Begonia* enhance their light harvesting for photosynthesis [49]. It may well be possible to mimic these systems to design nanomaterials to emulate these natural photonic structures and to modulate how light is received by plants

Recent advances have begun to demonstrate that nanoparticles (NPs) can be designed taking inspiration from proven transgenic and naturally-occurring routes to interact with photosynthesis and photo-protection resulting in their augmentation and much needed boosts in crop yield [50]. This expanding field has been labelled by some as “plant nano-bionics”. If similar enhancement to transgenic and natural systems are realised using NPs, it may usher in the dawn of a desperately-needed second “green revolution”. This potential alone provides a significant driver for the exploration and design on nano-bionic systems for agriculture.

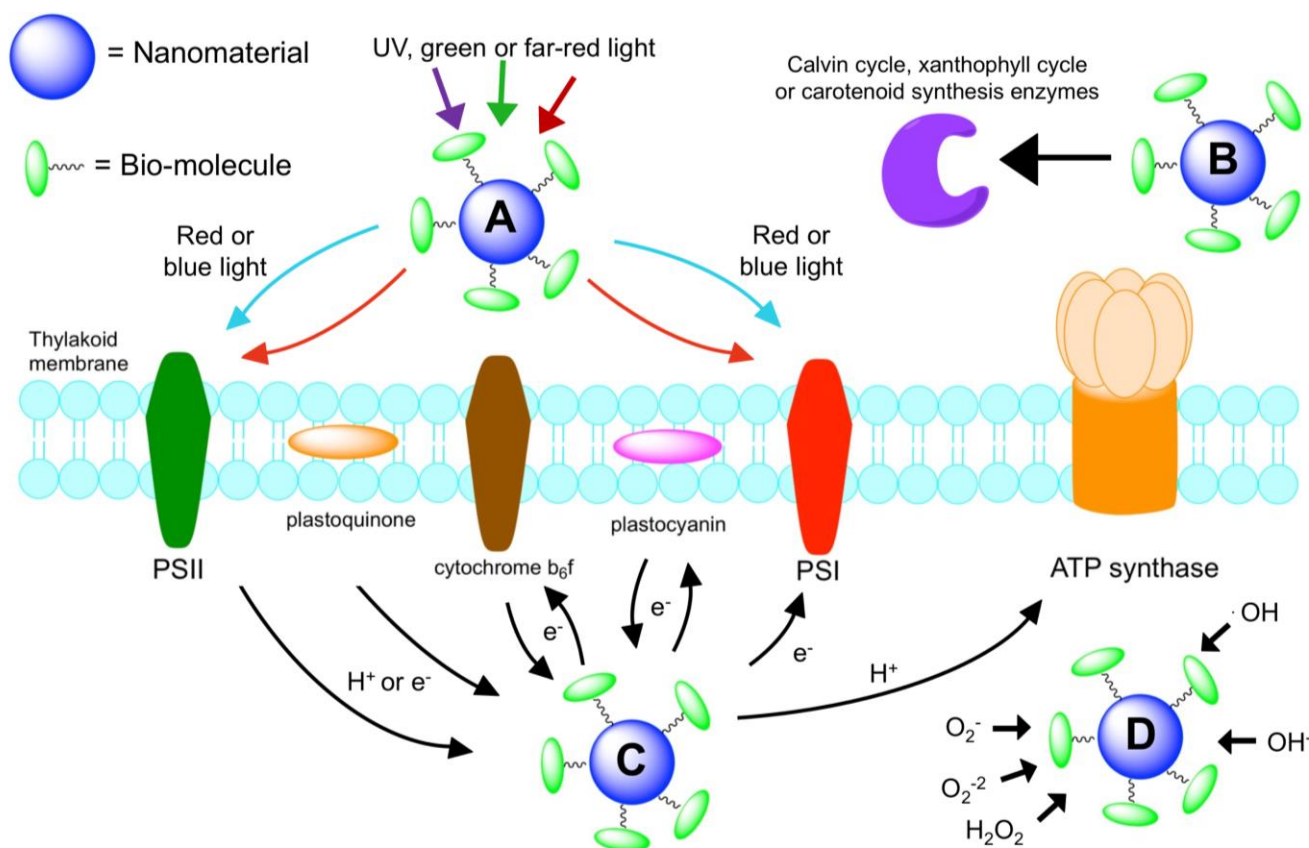
## **The case for plant nano-bionics**

Nanomaterials is a term coined to describe an exceptionally diverse class of materials, in terms of their shape and composition, that are essentially only unified by their size. For a material to be regarded as a nanomaterial it must have one of its physical dimensions between a nanometre and a micron in length, therefore it may be used to refer to everything from metre wide sheets of graphene through to metal clusters consisting of 10s of atoms. The nanoscale size range is significant because on sub-micron length scales, material properties often markedly diverge from those of their bulk counterparts which often resulting in unexpected and novel properties. The disparate characteristics that are exhibited at the

nanoscale primarily occur for two reasons: the extraordinary surface area to volume ratio of nanoparticles compared to their bulk counterparts, for example causing radically increased chemical reactivity; and quantum effects resulting in tuneable absorption and fluorescence spectra based on particle diameter, due to the confinement of excitons in quantum dots (QDs). Nanomaterials provide access to these described unique and often desirable properties from readily available bulk materials which makes the design of nanomaterials for agriculture an exciting and promising prospect that may provide otherwise unattainable results.

There are several routes for the design of NPs to interact with photosynthesis, some of which are illustrated in Figure 1. The engineering of NPs with unique properties that are disparate from bulk material to enable bespoke properties for specific interactions is one approach. This type of functionality may also be achieved by the design of the surface chemistry on the NP. It has previously been demonstrated that the surface-functionalisation of NPs with biomolecules such as carbohydrates can dramatically reduce the observed toxicity of NPs in mammalian cell systems [51–56]. Many NPs have been designed to have low or negligible toxicity to humans [57,58], which is probably the most desirable property when considering designing NPs for agriculture.

For light harvesting applications (Figure 1, A) it is also possible to tune the electronic structure of the NPs by changing their size, in the case of QDs [59], or careful choice of starting materials when synthesising some carbon nanomaterials [60].



**Figure 1:** Potential advantageous interactions between NPs and photosynthetic infrastructure. (A) The NP acts as additional light harvesting antenna, potentially Stokes-shifting non-photosynthetically active illumination into the photosynthetic spectrum or purely acting as a reflector; (B) the NP enhances or accelerates the kinetics of key enzymatic activity; (C) the NP acts as either an electron or proton transporter; (D) the NP acts as a sink for the otherwise damaging ROS. Here it is also suggested that surface biomolecule functionalisation may enhance the interactions and reduce toxicity.

## Established nanomaterial – photosynthetic interactions

As a response to the discovery of new forms of NPs as well as their presence in the environment, researchers have begun experimenting on how different NPs affect plant systems and whether this can be used to amplify productivity. Early studies of NPs in plants predominantly focused on the toxicological effect of metal oxide NPs leaching into soils. The effect of these studies concentrated on the effect of silicon dioxide NPs on plants, and investigated the impact on the growth of larch seedlings, which showed an increase in root growth, possibly evidence of the silicon dioxide NPs causing a starvation response [61]. The effects of cerium oxide ( $\text{CeO}_2$ ) have received more attention, and their uptake by *Coriandrum sativum* (coriander) from spiked soil has been shown to have a negligible effect on biomass production, however similar to the silicon dioxide NPs, elongation of the roots was observed [62]. It has also been

shown that when CeO<sub>2</sub> NPs are in soils they can reach the food chain and even be present in the next plant generation [63]. While these physiological effects are not of interest for enhancing photosynthesis, CeO<sub>2</sub> NPs have been demonstrated to be effective at ROS scavenging [64,65]. This feature may provide a significant role as an additional treatment to deal with increased ROS production that is triggered by some NPs [50]. CeO<sub>2</sub>, lanthanum oxide, gadolinium oxide and ytterbium oxide NPs have been shown to be taken up from soil by wheat, lettuce and rape. Interestingly none of these were shown to enhance root length, highlighting that NPs effects on plant systems are highly species dependent [66]. This is further exemplified in the plant uptake and distribution studies of functionalised gold NPs in several plant species, whereby it was demonstrated that that uptake is dependent not only on the species, but also on the surface charge of the NPs. It is important to note that this species dependence for NP-uptake has been supported by other subsequent work screening NP uptake in crop species [67–69].

Recent work has demonstrated that application of NPs in plants offer a promising method for engineering light-harvesting photosynthetic hybrids similar to the mechanism indicated in Figure 1, A. One of the earliest investigations of the possible interactions between NPs and photosynthesis demonstrated that energy transfer from the QDs as artificial light harvesting antennae which transfer energy to reaction centres, [70]. This has been approached using silver and gold NPs demonstrating that if the plasmon resonance is chosen correctly it will quench chlorophyll fluorescence [71,72] and furthermore, titanium oxide NPs have been shown to enhance energy transfer away from PSII, which may increase the energy conversion efficiency for PSII thus allowing increased light absorption [73]. None of these approaches have yet been demonstrated to enhance crop yields.

## **Recent advances of carbon nanomaterials *in planta***

Some of the most successful work using NPs to directly interact with photosynthesis has been using modern carbon-based nanomaterials, specifically carbon nanotubes (CNTs) and carbon dots (CDs).

CNTs are formed from cylinders of graphene and can be a single cylinder or several concentric cylinders, known as single-walled and multi-walled CNTs respectively. Their unique characteristics were first realised shortly after their discovery in 1991 [74]. CNTs have astounding properties that have enabled their use in electronics, sensing, light-emitting diodes, transistors and drug delivery [75–81] however these materials have been shown to be toxic in some forms [82,83]. One of the seminal works in the area of “plant nanobionics” was described by Giraldo *et al.* where they established incorporation of CNTs through the thylakoid membranes within the chloroplasts enabling the CNTs to increase ETR in *Arabidopsis* leaves and in isolated chloroplasts [50]. It should be noted this was achieved by the penetration of the CNTs through thylakoid membranes and with the addition of CeO<sub>2</sub> NPs as a ROS scavengers. CNTs have also been shown to affect root elongation and germination [84], can be



internalised by plant cells, and increase the concentration of ROS [85,86]. However, recent work has demonstrated that CNTs may not impact germination and development of wheatgrass [87] and have a positive impact on the effective yield of tomato plants, leading to an increase in flowering without decreasing leaf production. CNTs have also been shown to enhance growth of both root and shoot in gram (*Cicer arietinum*) [88]. All of this clearly highlights the species dependence of the impact of CNTs. Despite these advances in the application CNTs to augment photosynthesis, their toxicity to both plants and humans may limit their potential uses in crop species.

The first CDs were produced in 2004 by the fragmentation of CNTs into orange fluorescent NPs [89] which has since prompted the development of a new class of NPs. CDs are described as quasi-spherical NPs consisting of crystalline-carbon domains. Since their discovery, water soluble CDs have been synthesised with fluorescence maxima throughout the visible part of the electromagnetic spectrum [90–93], however initial synthetic preparations were expensive and laborious. The microwave synthesis of water-soluble CDs from cheap starting-materials such peptides, carbohydrates and generally a diverse range of carbon sources [94,95] has provided a low-cost, rapid alternative to these nanomaterials [60,90,91,96–98]. Furthermore, recent advances in the synthesis and surface-functionalisation of CDs have enabled them to surpass, in some instances, traditional cadmium based QDs as a fluorescent NP for biological and chemical applications because of their low toxicity and photo-stability. This also suggests that CDs provide a viable option for large agricultural applications of NPs as they are often produced by heating of carbon sources similar to the waste biomass that is readily available to agriculture.

Despite this increase in research into the application of CDs surprisingly little is known about the origins of their fluorescence and their structure [99]. Many studies have investigated the energy structure and photoluminescence mechanisms of CDs and concluded that CDs do not present fluorescence due to quantum confinement, as per QDs, moreover, these fluorescent NPs should be considered as nano-scale assemblies of fluorophores [99,100]. The fluorescence spectrum is broad, and has been shown to originate from the  $sp^2$  and poly-aromatic domains on the surface of the CDs [101,102]. Typically CDs present large Stokes shifts and are photo-stable [103,104]. We have recently demonstrated, counter to prior assumptions, that biomolecule-functionalisation does not result in a homogenous corona and dramatically changes the electronic structure of the NPs [105].

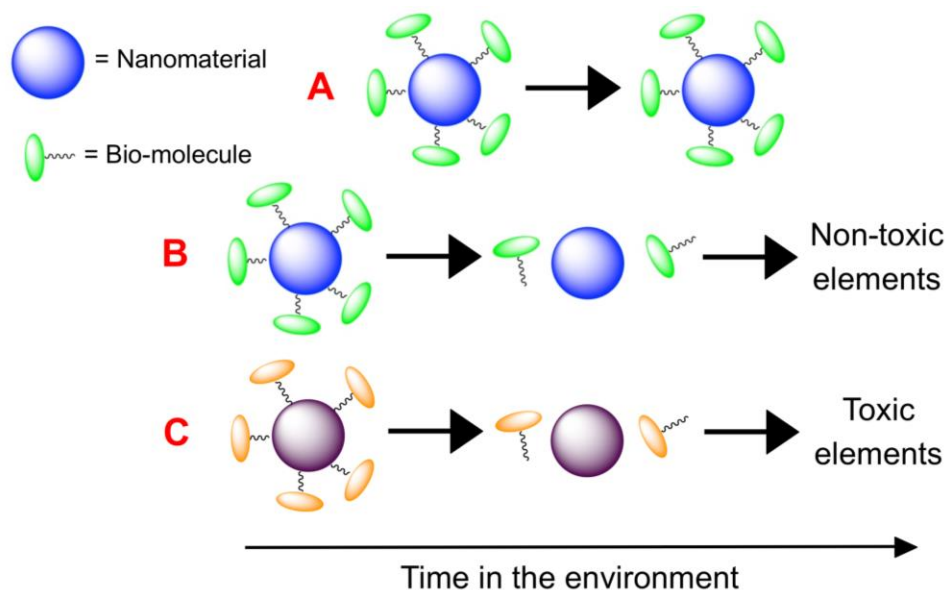
These recent developments suggest that CDs are able to circumvent the previous limitations of nanomaterials due to their apparent toxicity and complex synthesis. This has already prompted researchers to utilise CDs for a plethora of biological applications, as fluorescent labels for organelles [106–108], for targeting cancer cells [109] and gene delivery [110].

Recently studies have focussed on whether CDs can be used to enhance photosynthesis, with the aim of increasing crop productivity. These lines of work began with the application of CDs to isolated

chloroplasts from mung beans. Rather amazingly, the CDs were shown to increase oxygen evolution and ATP synthesis by promoting the electron transport pathway [111] which could be considered the first evidence that CDs enhance photosynthesis. This has since prompted further research *in planta* focused on the uptake and transport of CDs through the shoots of mung beans, showing an increase in root and shoot length following CD addition but there is little evidence that current CD applications would increase crop yield [112,113]. These interesting results raise questions about why enhanced photosynthesis in this case has not translated into biomass production. One reasonable explanation might be that CDs can provide a route to the beneficial effect of enhancing photosynthesis but has mitigating negative effects, similar to the enhanced ROS production observed with CNTs. It may be possible to modify the surface chemistry of the CDs using techniques such as biomolecule-functionalisation to reduce the impact of the negative side-effects.

## **Nanomaterials and the environment**

Rightly, one of the common concerns about the use of NPs to approach food security problems is the inevitable leaching of NPs into the environment and what the repercussions of this could be [114–116]. Clearly if NPs are to be used to augment crop, they must also have acceptably low toxicity to humans, plants and the environment. This may initially be approached by modification of the surface-chemistry of the NPs which has already shown promise in human cytotoxicity studies [54,56]. Yet ultimately the stability of the NPs and their possible decomposition products must be of concern and the use of NPs must be regarded as pointless if the breakdown products of the NPs in the environment are themselves toxic. This is clearly relevant for several classes of NPs, for example QDs where surface-functionalisation can initially reduce their observed toxicity however they often still contain a core formed of exceptionally toxic elements such as Cadmium and the effect of their breakdown in the environment could be disastrous[54]. Currently there has been little effort to explore these long term environmental effects and therefore if we are to utilise NPs in agriculture it is imperative to synthesise stable NPs or NPs with acceptably biologically-inert breakdown products. There are three simple potential fates of a NP in the environment: the NP remains stable and its toxicity does not change (Figure 2, A); the NP breaks down into non-toxic components (Figure 2, B); or the NP breaks down into toxic components (Figure 2, C). We call for the development of a standardised method of determining which of these three pathways a NP takes. For responsible research and innovation into NPs, it is essential a secure approach to assessing the resulting risks of the use of these NPs in food that goes beyond traditional cytotoxicity studies and assesses the long-term humanitarian and environmental implications and fate of the NPs is implemented.



**Figure 2:** Scheme of the potential breakdown pathways of NPs in the environment. (A) The NP is stable in the environment and retains its initially observed toxicity; (B) the NP breaks down in the environment into non-toxic elements; (C) the NP breaks down in the environment into toxic elements.

Whilst concern about the leaching of anthropogenic NPs into the environment and its ramifications is certainly well placed, and should play a key role in responsible research into NPs, it is also important to consider that NPs are already ubiquitous in nature [115,116]. As a consequence, perhaps the question should not be whether NPs will interact with agriculture but rather regarding the magnitude of the effect on agriculture; how current anthropogenic NP production will change that; and whether this can be harnessed to boost crop yields to address food security.

NPs are most abundant in the atmosphere, in the predominant form of amorphous-carbon, although they can contain metals. NPs are expelled by high-energy events such as volcanic eruptions and forest fires. Examples of these high energy events where the NPs have been investigated include the 2010 eruption of Eyjafjallajökull in Iceland [117,118] and forest fires in North America and Africa [119–121]. These processes may have previously had a powerful effect on agriculture as traditionally humanity has farmed volcanic ash or forest-fire stricken land due to its fertile nature. Whilst this is an interesting, and currently unstudied, line of inquiry in an anthropological context, most modern farming does not occur on burnt soil or volcanic ash. However, this still holds modern relevance as it has become increasingly popular to spread pyrolysed biomass, known as biochar, onto soil to increase crop yield [122]. This may be inadvertently spreading amorphous-carbon NPs into crop and the food supply with unquantified effects.

Although high-energy events account for the largest productions of NPs, there are a plethora of other natural processes that produce smaller quantities of a more exotic range of NPs for example:

magnetotactic bacteria produces iron oxide NPs in a variety of morphologies [123–125]; sunlight driven reduction of silver ions to silver NPs [126]; rare-earth metal NPs can even be found in the rivers produced by the melting Greenland ice sheet [127]. Although it is possible that these NPs may have varied and powerful interactions with agriculture, their production is not significant enough to be of concern.

There are a wide range of industrial processes that result in the inadvertent anthropogenic synthesis of NPs. Although they were probably present before, anthropogenic production of NPs has dramatically increased since the late 18<sup>th</sup> century with the industrial revolution, predominantly due to the burning of fuels. As a consequence of the near random way in which these NPs have been synthesised and the wide range of initial materials that have been used, these materials are poly-disperse and primarily consist of carbon, nitrogen and sulphur compounds as well as metals and metal oxides [128,129].

There is already widespread concern about the environmental impact and immediate toxicity of these NPs [114,116,128,130]. Yet it remains relatively unstudied whether this large-scale anthropogenic production of NPs may already be interacting with agriculture and that the fate of many of these NPs may well be within our food supply and ultimately us. Without this knowledge it is impossible to inform and provide guidance to the public and policymakers regarding the safety and applications of different NPs [115]. It is imperative that this is achieved with due reverence to two issues: prevention and reduction of risk to the public and the environment; and the prevention of overregulation with detrimental effects similar to those observed with genetic modification in Europe [131–133].

## Conclusions

There is a clear demand to greatly increase crop-productivity, without which we can expect food shortages. Augmenting how plants absorb and utilise light offers a route to achieving these required increases. NPs have been shown as a new, powerful and promising tool to augment photosynthesis *in planta* that is yet to be fully harnessed. This review argues for the expanded study of the existing interactions between NPs and agriculture as well as effort into engineering these interactions to realise increased food production.

Currently CNTs and CDs appear to have the most potential, both have been demonstrated to enhance photosynthesis but both also seem to provide other negative processes that pacify their capacity to increase crop yields. With careful design, it may be possible to produce more efficacious NPs that successfully realise positive impacts on agriculture. These NPs must also remain viable for large-scale agricultural applications without presenting unacceptable toxicity to us or the environment. Thus the field of “plant nanobionics” presents an exciting and expanding new area of research that offers real promise.

If NPs are to be widely used on an agricultural scale, it is vital that the consequences of synthetic NPs being poured into the environment are known and the public and policymakers are well informed.

As a consequence, much more work into eco-toxicology of NPs is still needed to fully evaluate their long-term impact and fate.

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## Author contributions

TAS, TAAO, MCG and HMW wrote the manuscript.

## Competing interests

The authors declare no competing financial interests.

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